

**REMARKS**

Claim 21 is amended and new claims 28-30 are added. Support for the amendment is found, for example, at page 5, lines 4-7, page 64, line 21, and the upper half of page 51.

Applicants note that new claim 28 corresponds to claim 24 as presented in the Preliminary Amendment filed on March 24, 2006, which was previously canceled. No new matter is presented.

Accordingly, upon entry of the Amendment, claims 21-23 and 25-30 will be all of the claims pending in the application.

Claims 21-23, 25 and 27 are rejected under 35 U.S.C. § 102(b) as being anticipated by Matsuoka et al (U.S. Patent No. 5,384,236).

Claims 21-23, 25 and 27 are rejected under 35 U.S.C. § 102(b) as being anticipated by Nagaoka et al (U.S. Patent No. 5,460,929).

Claims 21-23, 25 and 27 are rejected under 35 U.S.C. § 102(b) as being anticipated by Miyayashi et al (U.S. Patent No. 5,543,282).

Claim 26 was "provisionally rejected" as obvious over JP 2000-181002; JP 11-119364; JP 51-59943; JP 54-32552; and JP 2001-133931.

Since this rejection is only provisional, Applicants do not comment thereon. English language equivalents or Abstracts of the "applied Japanese patents" are submitted herewith as follows:

Attachment A: English Abstract for JP 2000-181002;

Attachment B: English Abstract for JP 11-119364;

Attachment C: GB 1504950 corresponding to JP 51-059943;

Attachment D: English Abstract for JP 54-032552; and

Attachment E: English Abstract for JP 2000-1133931.

Claim 21 is amended herein to recite that the silver halide color photosensitive material contains a coloring coupler and that a compound other than the coloring coupler is used to increase the speed of the silver halide color photosensitive material and is represented by the formula (C). This makes it quite clear that the compound represented by general formula (C) of claim 21 is **not used as the coloring coupler** but rather is used to increase the speed of a silver halide color photosensitive material containing another coloring coupler.

Further, the present invention is directed to a method of increasing the speed, not directed to a silver halide color photosensitive material containing a conventional coloring coupler.

Applicants respectfully submit that the prior art which the Examiner has relied upon, namely, Masaoka, Nagaoka and Mihayashi, clearly teaches usage as coloring couplers, and, as a consequence, by amending claim 21 as discussed above, Applicants have distinguished the prior art relied upon by the Examiner.

It is believed that Applicants have responded to all actual rejections, and Applicants respectfully request withdrawal.

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

Amendment under 37 C.F.R. § 1.114(c)  
U.S. App. Ser. No. 10/809,912

Q80656

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,

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WASHINGTON OFFICE

**23373**

CUSTOMER NUMBER

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Registration No. 24,513



Date: May 30, 2006

## Attachment A

## PHOTOGRAPHIC RECORDING ELEMENT

**Patent number:** JP2000181002  
**Publication date:** 2000-06-30  
**Inventor:** MASKASKY JOE EDWARD; REED KENNETH J;  
SCACCIA VICTOR P; FRIDAY JAMES A  
**Applicant:** EASTMAN KODAK CO  
**Classification:**  
**- international:** G03C1/005; G03C1/04; G03C1/10; G03C1/12;  
G03C7/30; G03C1/005; G03C1/04; G03C1/10;  
G03C1/12; G03C7/30; (IPC1-7): G03C1/035; G03C1/04;  
G03C1/08; G03C7/00; G03C7/30  
**- european:** G03C1/005T; G03C1/04; G03C1/10; G03C1/12;  
G03C7/30L  
**Application number:** JP19990357669 19991216  
**Priority number(s):** US19980213766 19981217

## Also published as:

 EP1011025 (A1)  
 US6187525 (B1)

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## Abstract of JP2000181002

**PROBLEM TO BE SOLVED:** To provide a photographic recording element which is very much improved in photographic characteristics than the conventional record elements. **SOLUTION:** This photographic record element comprises a support body and at least one of dye image forming layers comprising (a) radiation sensitive silver halide grains, (b) a sensitizer for (a), (c) a deflocculant for (a), and (d) at least one kind of dye image-providing coupler, and the silver halide grains have principal faces 111} and have a silver bromide content of 50% or larger of the total silver halide, and (3) flat silver halide grains occupy 50% or more of the projection areas of the total silver halide grains, and the sensitizer contains a fragmentizable electron-donor sensitizer and the deflocculant is a monoequivalent image dye-producing coupler.

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## Attachment B

**SILVER HALIDE PHOTOGRAPHIC SENSITIVE MATERIAL**

**Patent number:** JP11119364  
**Publication date:** 1999-04-30  
**Inventor:** HIOKI TAKANORI  
**Applicant:** FUJI PHOTO FILM CO LTD  
**Classification:**  
- international: **G03C1/12; G03C1/12; (IPC1-7): G03C1/12**  
- european:  
**Application number:** JP19970283813 19971016  
**Priority number(s):** JP19970283813 19971016

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## Abstract of JP11119364

**PROBLEM TO BE SOLVED:** To obtain a photosensitive material high in sensitivity and small in fog and superior in storage stability by incorporating a specified compound. **SOLUTION:** The photosensitive material contains at least one of the compounds represented by formulae I and II and at least one of the compounds represented by formula III, and in the formulae I-III, Z is a group adsorbable to silver halide or a light-absorbing group; L is a bonding group containing at least one C, N, S, or O atom; k1 is 0-4; k2 is 1-4; k3 is 0 or 1; XY is a partial structure composing an electron donative group and it has an oxidation potential of 0-1.4 V and X is an electron donor and Y is a releasable group except H atom; each of k4 and k5 is 1-4; k6 is 0 or 1; and each of A1 and A2 is H atom or a univalent substituent and each may combine with each other to form a ring.

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# AQUEOUS POLYMER LATEXES CONTAINING HYDROPHOBIC MATERIALS

Attachment C

Patent number: JP51059943  
Publication date: 1976-05-25  
Inventor: TSUANGU JAN CHEN  
Applicant: EASTMAN KODAK CO  
Classification:  
- international: *A01N25/10; C08J3/215; C08L33/06;  
G03C1/04; G03C7/388; A01N25/10;  
C08J3/20; C08L33/00; G03C1/04;  
G03C7/388; (IPC1-7): C08J3/20; G03C1/06*  
- european: *A01N25/10; C08J3/215; C08L33/06;  
G03C1/04; G03C7/388P*  
Application number: JP19750112519 19750917  
Priority number(s): US19740506919 19740917; US19750575689  
19750508

Also published as:

GB1504950 (A)
FR2285431 (A1)
DE2541274 (A1)
CH616440 (A5)
IT1044391 (B)

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☐ Abstract not available for JP51059943

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# PATENT SPECIFICATION

(11) 1 504 950

1 504 950

- (21) Application No. 37436/75      (22) Filed 11 Sept. 1975
- (31) Convention Application No. 506919
- (32) Filed 17 Sept. 1974
- (31) Convention Application No. 575689
- (32) Filed 8 May 1975 in
- (33) United States of America (US)
- (44) Complete Specification published 22 March 1978
- (51) INT CL<sup>1</sup> C08J 3/20
- (52) Index at acceptance  
C3L DG
- (72) Inventor TSANG JAN CHEN



## (54) AQUEOUS POLYMER LATEXES CONTAINING HYDROPHOBIC MATERIALS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods of making aqueous loaded polymer latexes, to photographic materials containing them and to certain loaded polymer latexes *per se*.

Several techniques have been used successfully and commercially heretofore to distribute hydrophobic compounds, particularly non-polymeric compounds such as photographic colour-forming couplers, ultraviolet absorbing materials and the like, fairly uniformly through layers of gelatin or other hydrophilic colloids in the manufacture of photographic products. One of the simplest of these techniques involves mechanically dispersing (i) the hydrophobic compound(s) in solid or liquid form through (ii) a hydrophilic colloid solution by first blending together (i) and (ii), and then passing the resulting blend several times through a high energy mill such as a colloid mill. This technique produces inferior dispersions (as compared to other conventional dispersion techniques), which inferior dispersions are often unstable. Also large amounts of energy are consumed by this technique to accomplish the desired degree of particle comminution and dispersion. The large consumption of energy is often accompanied by heat buildup, or undesirable localized heating and by undesirable chemical degradation of some of the ingredients involved.

Another technique for distributing hydrophobic compounds through a hydrophilic colloid solution or dispersion (which is subsequently coated and dried to yield a solid hydrophilic colloid layer in which the hydrophobic compounds are dispersed) is described in U.S. Patents 2,304,940 and 2,322,027. This technique involves initially forming a solution by dissolving the hydrophobic compound(s) in oils or higher boiling solvents and then dispersing the resulting oily solution into the hydrophilic colloid solution or dispersion. Variations of this general technique have included the use of a lower molecular weight auxiliary solvent such as ethyl acetate or a lower molecular weight ketone to aid in the solubilization of the hydrophobe in the oily solvent, like for example the method described in U.S. Patent 2,801,171. For the manufacture of colour photographic materials containing, incorporated therein, ballasted colour-forming couplers, techniques involving the use of such oily, higher boiling, so-called coupler solvents have become widespread commercially. However, the techniques of dispersion of such coupler solutions require a high energy milling step (to obtain the desired degree of dispersion and particle size), which can result in some undesired degradation of some of the ingredients in the milled product. Also, such a milling step is both time consuming and expensive.

Some prior uses of latexes (latices), for example, involved the use of latexes merely as a source for a polymeric ingredient in the coated layers. Conventional latexes have often been simply blended into a photographic emulsion which usually contained gelatin, silver halide and the usual photographic addenda. When organic solvents and hydrophobic compounds such as colour-forming couplers were used heretofore in conjunction with synthetic polymers in the manufacture of coating com-

positions, often both the hydrophobe and the polymer were dissolved in the solvent prior to being formulated into the remainder of the coating compositions. (See for example, U.S. Patents 3,518,088, 2,269,158 and 3,619,195). In one patent, U.S. 2,772,163 (British Specification 759,409), certain latexes were used in conjunction with alkali soluble, ballasted colour-forming couplers of the type described in U.S. Patent 2,376,679. Such couplers were dissolved in alkaline solutions, which couplers could be precipitated from solution upon neutralization of the alkali. Among other differences, the latex used differs from those of the present invention, in that it is not a loadable latex (as defined hereinafter). Also, the present invention is much more broadly useful with regard to nature of the hydrophobic materials and the present process makes it possible to incorporate a significantly large amount of hydrophobic material into polymeric latex particles, as compared to the process of U.S. Patent 2,772,163.

According to the present invention there is provided a method of making an aqueous loaded polymer latex, of which the dispersed phase comprises a polymer and a hydrophobic compound (as defined herein), which comprises the step of adding to a solution of the hydrophobic compound in a water-miscible organic solvent (as defined herein), an aqueous loadable polymer latex (as defined herein) and, if required, at least sufficient additional water to cause the hydrophobic compound to become insoluble in the aqueous medium so formed so that the loaded polymer latex is formed.

The loaded polymer latexes are polymer latexes in which the dispersed or discontinuous phase consists essentially of particles of a synthetic polymer and one or more hydrophobic compounds or hydrophobes as they are sometimes referred to herein. It is believed that the hydrophobic compound is associated with the polymer particles both on the surface of the particles and in the interior thereof.

The present invention also provides an aqueous loaded polymer latex of which the dispersed phase comprises a loadable polymer (as defined herein) and a hydrophobic compound (as defined herein) wherein the particles of the dispersed phase have an average diameter of 0.02 to 0.2 micron.

The preferred polymer latexes will hereinafter be referred to as photographically useful loaded latex compositions and they comprise compositions which may be employed in the manufacture of photographic materials.

It is believed that many of the valuable results that can be obtained by practicing the present invention directly result from the unique physico-chemical changes that occur (with respect to the hydrophobic material and the polymeric latex particles) during the present process. Thus, as the aqueous latex is gradually introduced into the solution of hydrophobe (in acetone, for example), the acetone solution gradually becomes more hydrophilic in character due to the incorporation of more and more water. At some point (depending on the particular type and quantity of hydrophobe and the particular type of water-miscible solvent that is used) the medium becomes so hydrophilic that the hydrophobe can no longer remain dissolved therein, and the hydrophobe begins to change to an undissolved state. By this time, there has been introduced into the acetone solution a large number of loadable polymeric latex particles as well as the water. These particles apparently swell at least to some slight extent in the presence of the acetone, thereby becoming so receptive to the hydrophobic material that, when the hydrophobe is forced out of solution in the acetone, in some as yet unexplained manner it is preferentially absorbed into the latex particles.

Thus, the process of this invention involves gradually increasing the hydrophilicity of a solution of a hydrophobe in a water-miscible solvent in the presence of uncoagulated, undissolved loadable polymer latex particles to a point at which substantially no hydrophobe remains dissolved in the water-miscible solvent phase. The increase in hydrophilicity is accomplished by adding water to the solution of hydrophobe in water-miscible solvent, preferably solely in the form of an aqueous loadable polymer latex.

It should be noted that some water can be present in the solution of hydrophobe material dissolved in water-miscible solvent, if desired, prior to the inception of the process step described immediately above, so long as the amount of said water is maintained below that level which would interfere with the desired mechanism described above, preferably below that level of water which causes a cloudy appearance in the hydrophobe/water-miscible solvent solution.

Some of the benefits that can result from practicing the present invention include:

- a. Hydrophobic organic compounds such as ballasted colour-forming couplers, ultra-violet absorbers, filter dyes, sensitizing dyes, other dyes, dye developing agents, silver halide developing agents, dye releasing agents, brighteners,



antioxidants and silver halide solvents can be uniformly distributed through a hydrophilic colloid-containing layer without the use of a high energy mill. As a result, satisfactory dispersions can be obtained by the process of this invention at considerably lower cost, and with substantially less undesired degradation of materials.

b. Some of the loaded latex compositions of this invention possess unique properties; for example, the hydrophobe portion thereof in some cases, appears to be more effective and/or more available for reaction.

c. When hydrophobic compounds which are ordinarily very susceptible to air oxidation are distributed into a loadable polymer latex in accordance with the present invention, a significant resistance to oxidation can be imparted to them apparently because they have been largely distributed into the particles of loadable polymer. Thus, the present process offers a means to distribute into hydrophilic colloid layers materials which, as a practical matter, could not be incorporated heretofore without excessive degradation. Examples of such materials which are susceptible to aerial oxidation include organic aromatic amino colour developing agents such as the *p*-phenylenediamines, the *p*-amino-phenols and certain pesticides.

d. In many instances, the present process makes it possible to incorporate considerably larger amounts of hydrophobe into particles of water insoluble polymer than was possible heretofore.

e. In some instances, the use of a loaded latex composition of this invention makes it possible to incorporate a hydrophobic material into a given layer in which the hydrophobic material had heretofore been incompatible or too reactive (due to the general reactivity of the hydrophobic material with other ingredients in the layer, for example). In such cases, use of the present invention can obviate the necessity for more than one layer on a substrate containing materials which would otherwise be too reactive to be contained in a single layer.

The water-miscible organic solvent used in the practice of this invention is one which:

- a. is miscible with distilled water at 20°C to the extent of at least about 20 parts by volume of solvent in 80 parts by volume of water;
- b. has a boiling point (at atmospheric pressure) above -10°C.
- c. does not detrimentally react chemically with the loadable polymer latex with which it is intended to be used; and
- d. does not dissolve more than 5 weight percent of such loadable polymer latex at 20°C.

Regarding requirement "c" for solvents useful in the practice of this invention, reaction between the solvent and polymer may be possible under certain circumstances, but it is believed to be unlikely. Examples of water-miscible organic solvents which may be used are acetone, ethyl alcohol, methyl alcohol, isopropyl alcohol, methyl ethyl ketone, tetrahydrofuran, N-methylpyrrolidone, dimethylformamide, dimethyl sulphoxide, and mixtures thereof. Of these, acetone, dimethylformamide and/or tetrahydrofuran are preferred when the hydrophobic material in question is soluble therein.

The term "loadable polymer latex" is employed herein to refer to those aqueous latexes which pass the following test:

#### Loadable Polymer Latex Test

At 25°C. slowly stir 250 ml of polymer latex containing 12-20 weight percent solids into an equal volume of acetone. The addition should take place over 1 minute at a steady, uniform rate, while the acetone is being stirred moderately. Discontinue the agitation and let the resulting blend stand at about 25°C for 10 minutes. At the end of that time observe the blend. Loadable polymer latexes are those which exhibit essentially no visible coagulation or settling out under these test conditions.

The preferred polymer latexes are compatible with gelatin solutions and in dried gelatin layers. The term "loadable polymer" as used herein refers to the polymer of a loadable polymer latex.

A preferred class of loadable polymer latexes have a discontinuous phase (polymer particles) which consists essentially of polymer polymerized from at least two ethylenic monomers, from 2 to 25 weight percent of which comprise a monomer containing a carboxylic acid or carboxylate or preferably a sulphonic acid or sulphonate group, and an aqueous continuous phase.

One preferred class of loadable polymers is a copolymer prepared from:

(a) 75 to 98 weight percent of a monomer of the formula:



wherein

R is hydrogen or an alkyl group having 1—5 carbon atoms,

R' is hydrogen or a methyl group and

R'' is an aliphatic group having 1—6 carbon atoms, and

(b) 2 to 25 weight percent of an ethylenic monomer containing a sulphonic acid or sulphonate group and having a molecular weight of at most 300.

A more preferred class of loadable polymers is a copolymer prepared from:

(a) 80 to 95 percent of a monomer of Formula I as defined above,

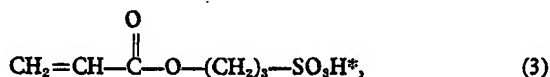
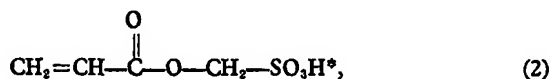
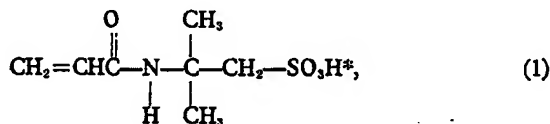
(b) 2 to 10 weight percent of an ethylenic monomer containing a sulphonic acid or sulphonate group and having a molecular weight of at most 300, and

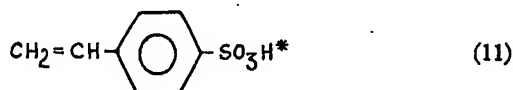
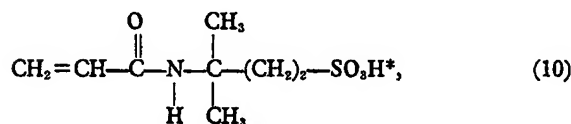
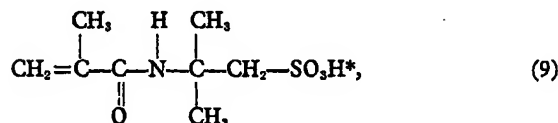
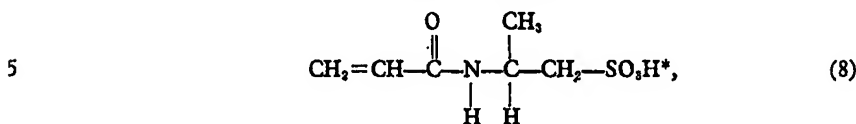
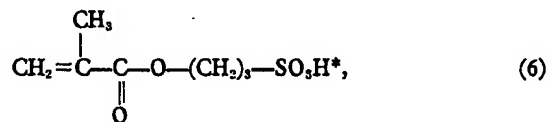
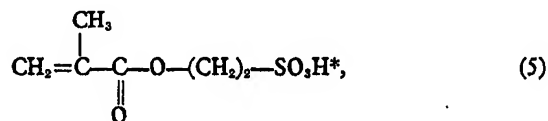
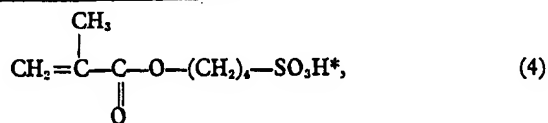
(c) 0.2 to 10 weight percent of an ethylenic monomer containing cross-linkable groups.

The crosslinkable groups contained in monomers (c) preferably comprise one or more groups which can be crosslinked by reaction with a photographically acceptable hardener, for example, an aldehyde, e.g. formaldehyde or succinaldehyde, or mucohalic acids, triazine chlorides, vinyl sulphones, e.g. bisvinyl sulphonylmethyl ether or aziridine. The preferred crosslinkable groups contain an active methylene group.

It should be noted that the ratios of monomers set out herein are based upon the relative weights of the monomers charged into the polymerization reactor in a conventional free radical polymerization process. Products from such reactions may vary to some extent in the ratios derived from the charged monomers for various reasons which are well known to those skilled in the art of manufacturing synthetic polymeric latexes. While loadable polymer latexes can be made from two, three, four or even more different monomers, those which are preferred for use in the practice of this invention are generally comprised of three or four monomers, depending upon the particular properties desired in the final product. Generally, polymer latexes that contain (as there dispersed phase) relatively soft particles are believed to be able to have distributed therein relatively more hydrophobe. On the other hand, where the best physical protection of the hydrophobe-containing layer (from abrasion for example) is desired, relatively harder loaded polymer latex particles should be used. Those skilled in the art of manufacturing polymers via free radical polymerization techniques are well acquainted with the types and amounts of monomers to utilize in order to produce latexes of relatively softer or harder polymers. The loadable polymer latexes may be prepared by free radical initiated reactions of monomers dispersed in an aqueous medium with one or more appropriate surfactants. See, for example, U.S. Patents 2,914,499, 3,033,833 and 3,547,899 and Canadian Patent 704,778.

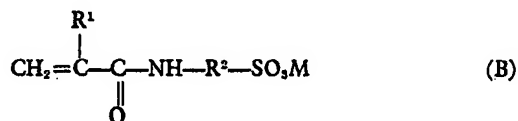
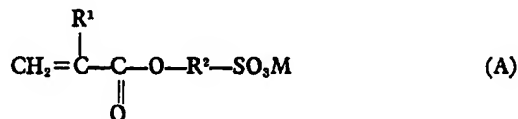
Monomers which are still further preferred for use in the manufacture of loadable polymer latexes are those wherein (i) the acrylic ester monomer is selected from the group consisting of methyl, ethyl, propyl and butyl acrylates and methacrylates, (ii) the hydrophilic ethylenic monomer is selected from those having a sulphonic acid (or water soluble salt thereof) group, preferably attached to a terminal carbon atom such as for example, those having the following structures:





(\* = in place of H can be an alkali metal cation, preferably Na or K, or ammonium ion).

wherein the generic formulae for the preferred subclasses of hydrophilic ethylenic monomers are:



wherein R<sup>1</sup> is methyl or hydrogen; R<sup>2</sup> is methylene, ethylene, 2-methylethylene, trimethylene, tetramethylene, or 2,2-dimethylethylene;; and M is ammonium, hydrogen or alkali metal cation, and (iii) the hardenable or crosslinkable ethylenic mono-

mer contains an active methylene hardenable group. Examples of such preferred crosslinkable ethylenic monomers include:

	(12) ethyl methacryloylacetate	
	(13) N-cyanoacetyl-N'-methacryloylhydrazine	
5	(14) 2-acetoacetoxyethyl methacrylate	5
	(15) N-(3-methylacryloyloxypropyl)cyanoacetamide	
	(16) 2-cyanoacetoxyethyl methacrylate	
	(17) N-(2-methacryloyloxymethyl)cyanoacetamide	
10	(18) ethyl alpha-acetoacetoxy methacrylate	10
	(19) 2-acetoacetoxypropyl methacrylate	
	(20) 3-acetoacetoxy-2,2-dimethylpropyl methacrylate	
	(21) N-(methacryloyloxymethyl)acetoacetamide	
	(22) N-t-butyl-N-methacryloyloxyethyl acetoacetamide	
15	(23) 2-acetoacetoxyethyl acrylate	15
	(24) 2-acetoacetoxy-2-methylpropyl methacrylate,	
	(25) N-allyl cyanoacetamide	

Some of these materials are described in U.S. Patents 3,459,790 and 3,488,708 and 2,808,331 and 2,940,956.

20	Examples of loadable polymer latexes include latexes which have solids content of at least 2 weight percent up to 20 weight percent and which contain the following components. Note that the monomers are set out below in the relative proportions by weight in which they are charged to the reactor during the manufacture of the latex.	20
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25	A. 85—sec. butyl acrylate 10—sodium 3-methacryloyloxypropane-1-methyl-1-sulphonate 5—2-acetoacetoxyethyl methacrylate	25
	B. 85—n-butyl methacrylate 10—sodium 3-methacryloyloxypropane-1-methyl-1-sulphonate 5—2-acetoacetoxyethyl methacrylate	
30	C. 70—n-butyl methacrylate 15—sodium 3-methacryloyloxypropane-1-methyl-1-sulphonate 10—methyl methacrylate 5—2-acetoacetoxyethyl methacrylate	30
35	D. 85—n-butyl acrylate 10—sodium 3-methylacryloyloxypropane-1-methyl-1-sulphonate 5—2-acetoacetoxyethyl methacrylate	35
	E. 85—n-butyl acrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate 5—2-acetoacetoxyethyl methacrylate	
40	F. 75—n-butyl methacrylate 10—methyl methacrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate 5—2-acetoacetoxyethyl methacrylate	40
45	G. 85—n-butyl methacrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate 5—2-acetoacetoxyethyl methacrylate	45
	H. 80—n-butyl methacrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate 10—acrylic acid	
50	I. 50—n-butyl methacrylate 40—styrene 10—sodium 2-acrylamido-2-methylpropane sulphonate	50
	J. 40—n-butyl acrylate 50—2-acetoacetoxyethyl methacrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate	
55	K. 60—2-acetoacetoxyethyl methacrylate 30—n-butyl acrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate	55
60	L. 50—N-butyl acrylate 40—2-acetoacetoxyethyl methacrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate	60

Additional loadable latex polymers include:

	M.	80—n-butyl acrylate 20—sodium 2-acrylamido-2-methylpropane sulphonate	
5	N.	95—n-butyl acrylate 5—sodium 2-acrylamido-2-methylpropane sulphonate	5
	O.	90—styrene 10—sodium 2-acrylamido-2-methylpropane sulphonate	
10	P.	85—ethylacrylate 10—3-methacryloyloxypropane-1-sulphonic acid, sodium salt 5—2-acetoacetoxyethyl methacrylate	10
	Q.	85—methyl acrylate 10—3-methacryloyloxypropane-1-sulphonic acid, sodium salt 5—2-acetoacetoxyethyl methacrylate	
15	R.	85—n-butyl acrylate 15—3-methacryloyloxypropane-1-sulphonic acid, sodium salt	15
	S.	70—n-butyl acrylate 20—sodium 3-methacryloyloxypropane-1-sulphonate 10—2-acrylamido-2-methylpropane sulphonic acid sodium salt	
20	T.	85—ethyl acrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate 5—2-acetoacetoxyethyl methacrylate	20
	U.	50—n-butyl methacrylate 40—styrene 10—sodium 2-acrylamido-2-methylpropane sulphonate	
25	V.	70—n-butyl acrylate 25—acrylamide 5—2-acetoacetoxyethyl methacrylate	25
	W.	85—methyl acrylate 10—sodium 2-acrylamido-2-methylpropane sulphonate 5—2-acetoacetoxyethyl methacrylate	
30	X.	85—n-butyl methacrylate 10—2-(methacryloyloxy)ethyltrimethylammonium methosulphate 5—sodium 2-acrylamido-2-methylpropane sulphonate	30
	Y.	85—ethyl acrylate 10—2-(methacryloyloxy)ethyltrimethylammonium methosulphate 5—sodium 2-acrylamido-2-methylpropane sulphonate	
35	Z.	85—n-butyl acrylate 10—2-(methacryloyloxy)ethyltrimethylammonium methosulphate 5—sodium 2-acrylamido-2-methylpropane sulphonate	35
	AA.	95—n-butylacrylate 5—p-styrene sulphonic acid, sodium salt	
40	BB.	90—n-butyl methacrylate 10—p-styrene sulphonic acid, sodium salt	40

From the foregoing description it is evident that many combinations of monomers can be used in the manufacture of loadable synthetic polymeric latexes in accordance with this invention. It must be pointed out, however, that many polymeric latexes are not loadable latexes as defined herein. For this reason it is recommended that before a given latex is assumed to be loadable it be tested by the procedure set out above. The use of this test is also recommended as a control procedure because of the relatively low level of batch-to-batch reproducibility that sometimes occurs in the commercial manufacture of polymeric latexes. A preferred method for manufacturing loadable latexes is described later below.

By the term hydrophobic compound as employed herein we mean a compound which must:

- |    |     |  |    |
|----|-----|--|----|
| 55 | (a) | be practically or essentially insoluble in distilled water at 25°C being less than 0.5 weight percent soluble,   | 55 |
|    | (b) | be soluble in acetone, ethyl alcohol, methyl alcohol, isopropyl alcohol, methyl ethyl ketone, tetrahydrofuran, dimethylformamide, N-methyl pyrrolidone or dimethylsulphoxide or a mixture of two or more thereof to the extent of at least 5 weight percent, and |    |
| 60 | (c) | be precipitated from solution in the water-miscible solvent upon the addition to said solution of up to an equal volume of water.  | 60 |

Although the particular identity of any hydrophobe meeting this definition is not

important with respect to the successful practice of the process of this invention, certain classes or types of hydrophobes result in products having unexpectedly valuable utility in the field of photography. Preferred hydrophobic compounds useful for this aspect of the present invention are ballasted colour-forming couplers, filter dyes, antifoggants, development modifiers, bleach modifiers, ultraviolet absorbing compounds, dye-releasing agents, e.g. redox dye releasing agents, developing agents and sensitizing dyes. Photographic materials in the preparation of which the process of the present invention is especially useful include, for example, image transfer materials, physical development materials, radiographic materials, dry development systems and colour-forming materials such as are described in "Product Licensing Index", Vol. 92, December 1971, pages 107—110, and in British Patent 923,045. Although this preferred embodiment is useful in the photographic industry, the present invention is not limited to photographic materials and processes, but is useful wherever it is deemed desirable to obtain a distribution of a hydrophobic material in a polymeric material. For example, the hydrophobe may be an insecticide, herbicide, miticide, hormone, vitamin or enzyme. It will be appreciated that the end use of polymeric latexes loaded with such materials may not involve coating a substrate. For example, the present process is useful in the manufacture of latex-type surface coating compositions such as latex paints, for example, wherein a hydrophobic UV absorber or chemical stabilizer (against oxidation) can be incorporated into the coating compositions by simply blending into an otherwise complete formulation a sufficient amount of one of the appropriate selected loaded polymeric latex compositions of this invention. Other uses are indicated below in the Examples.

The amount of hydrophobe which can be present in intimate association with the latex particles is preferably in the range from 2 to 300 parts or even more, more preferably from 25 to 200 parts, by weight per 100 parts by weight of polymer. It is still further preferred that the weight ratio of hydrophobe to polymer is from about 1:20 to about 1:1, i.e. from 5 to 100 parts by weight hydrophobic compound per 100 parts by weight of polymer.

In connection with the photographic art, particularly preferred hydrophobes include hydrophobic ballasted colour-forming couplers which can react with oxidized organic aromatic primary amino colour developing agents to form a dye. Examples of such couplers are couplers of the ketomethylene, pyrazolone, phenolic or naphtholic type are well known to the photographic chemist and are described in detail in some of the publications referred to in Product Licensing Index, Vol. 92, page 110, December, 1971.

Some hydrophobic, ballasted couplers that can be used in the practice of this invention are described in U.S. Patents 2,983,608; 3,252,924; 3,311,476; 3,277,550; 3,277,155; 2,778,658; 3,253,924; 3,447,928; 3,408,194; 3,476,563; 3,253,294; 3,458,315; 2,423,730; 3,277,554 and 3,703,375. Another class of hydrophobic materials useful in the practice of this invention are hydrophobic ultraviolet absorbing compounds such as disclosed in Product Licensing index, Vol. 92 109 (1971) and in U.S. Patents 3,687,671; 3,706,700; 2,739,888; 3,652,284; 3,468,897; 3,004,896; and 3,253,921.

Some hydrophobic dyes that can be used in the practice of this invention are described in U.S. Patents 3,652,284; 3,486,897; 2,751,298 and 3,506,443 and Product Licensing Index Vol. 92, pages 108—109, December 1971. Some dye image-forming materials useful in the practice of this invention are described in Canadian Patent 602,607; U.S. Patents 3,443,939; 3,443,940; 3,443,941; 3,725,062; 3,415,644; 3,415,645; 3,415,646; 3,647,437; and 3,635,707 and Belgian Patents 757,959; 757,960; 810,195 and 788,268.

Many hydrophobic developing agents that may be used in the practice of this invention are described in Product Licensing Index, Vol. 92, page 110 (1971) and in U.S. Patents 3,801,321; 3,672,896; 3,679,426; 3,672,904 and 3,751,249.

The photographic film products containing the loaded latex compositions of the present invention can readily be identified and distinguished from conventional film products containing physical mixtures of polymer hydrophobe by the fact that the polymeric particles in the film products apparently retain their identity as evidently being derived from the latex even after layers containing them have been dried. Thus, the hydrophobe is apparently distributed in the compositions of this invention fairly uniformly throughout the particles of polymer and apparently remain distributed through such particles, even though the loaded latex particles may be dispersed through one or more layers of hydrophilic colloid containing other materials, such as silver halide and the like. The identification of products prepared in accordance with the present invention involves the determination (a) that the particles were

evidently derived from a latex, and (b) that the hydrophobic material remains physically associated with the polymeric particles in the coated articles being analyzed (possibly as a solid solution of hydrophobe in polymer). Isolation of the particles, determination of the identity of the polymer, identification of the polymer as being latex derived, and determination of the identity, presence and amount of hydrophobe in the particles is within the capability of the skilled analytical chemist.

It is of special interest, in this respect, that certain hydrophobes can effect changes in the glass transition temperature ( $T_g$ ) of the loadable polymeric material when the hydrophobe is present at a sufficient level (depending upon the relative concentrations of loadable polymer and hydrophobe and their respective  $T_g$ 's). That certain hydrophobes can influence or change the the natural or expected  $T_g$  of the discontinuous phase of some of the loadable polymer latexes is evidence that in the photographically useful loaded latex compositions of this invention the hydrophobe is distributed through the polymer particles which make up the dispersed phase of such compositions.

Actually the measurement of the  $T_g$  of dried loaded latex compositions represents one method for identifying some of the preferred loaded polymeric latex compositions of this invention. Thus, a large number of such preferred compositions have  $T_g$ 's which differ from the initial  $T_g$  of the loadable latex polymer by at least  $5^\circ\text{C}$ . The reason that some of such preferred loaded latex compositions do not have  $T_g$ 's that differ by as much as  $5^\circ\text{C}$ . from the natural  $T_g$  of the latex polymer is because certain of the hydrophobes may have a glass transition temperature very similar to that of the particular latex polymer, or that the relative quantity of hydrophobe in the loaded latex particles is fairly low. Since the  $T_g$  of a homogeneous combination of materials must be between the  $T_g$ 's of the pure materials, it follows that not all of the loaded latex compositions made in accordance with the process of this invention can exhibit  $T_g$ 's which differ from the natural  $T_g$  of the loadable latex polymer by at least several degrees can be used as one means for identifying compositions as having been manufactured in accordance with the present invention.

Methods for measuring  $T_g$ 's are well known. A preferred method involves the continuous monitoring of the temperature of a test sample in a conventional differential thermal analysis apparatus (compared to the temperature of a blank "control") while heat is gradually added to the sample holder. The temperature corresponding to the midpoint of the baseline shift characteristic of the change in specific heat associated with glass transformation is the  $T_g$  of the test sample. The accompanying drawing illustrates this characteristic. Curve A represents the  $T_g$  curve for a loaded polymer latex (having a natural  $T_g$  of  $-42^\circ\text{C}$ ) into which 40 weight percent of a cyan colour-forming coupler (having a natural  $T_g$  of  $+39^\circ\text{C}$ ) has been incorporated by the present process. Note that in curve A, the  $T_g$  of the loadable polymer latex/colour-forming coupler composition is about  $-15^\circ\text{C}$ . Curve B which is presented for comparison, is the differential thermal analysis curve for a sample of a heterogeneous (physical) mixture of the latex and coupler (used for Curve A), whereby the materials were simply mixed together and then dried. The melting endotherm of crystalline coupler (at about  $135^\circ\text{C}$ ) is evident from Curve B, indicating the presence of a heterogeneous latex/coupler composition. Gelatin was present in both test samples used in the acquisition of the data for curves A and B. The presence of the gelatin is evidenced by the small  $T_g$  (for gelatin) at about  $+60^\circ\text{C}$  in both curves A and B in the drawing, and from the gel-sol transition noted at about  $+93^\circ\text{C}$ .

Some of the valuable results from practicing the present invention are believed attributable to the extremely small particle size of the resulting loaded latex dispersions of hydrophobic materials through the hydrophilic colloid layers of gelatin-containing photographic emulsions and the like. Thus, whereas the size of coupler dispersion particles (wherein colour-forming coupler is dissolved in high boiling solvent and dispersed into the emulsion via a high energy colloid mill) in conventional photographic emulsions is typically in the range of from 0.3 to 0.9 microns or more in diameter, the particles of the photographically useful loaded polymeric latex compositions of this invention are about an order of magnitude smaller, being within the range of from 0.02 to 0.2 microns, and preferably from 0.02 to 0.08 microns in diameter, even though the latex particles may have been "swelled" to some extent by the incorporation of a relatively large proportion of hydrophobic material. For example, in one experiment involving a loadable latex as set out in Example 3 below, the average diameter of charged latex particles was swelled to about 0.186 microns (from an average diameter of 0.117 microns initially) by the incorporation of

an equal weight of cyan colour-forming coupler, based on the dry weight of polymer in the latex.

Such a very small particle size may account at least partially for the observation that the use of the loadable polymeric latex/colour-forming coupler compositions of this invention results in the formation of photographic hydrophilic colloid layers having a much more uniform distribution of dye therethrough than has heretofore been observed. It is believed that the particular physico-chemical condition of the colour-forming coupler material in such coupler-loaded polymeric latex compositions also contributes in some as yet unexplained way to such valuable results. For example, it is believed surprising that photographic materials containing layers of emulsions which in turn contain coupler-loaded polymeric latex compositions of this invention (and essentially no high boiling conventional coupler solvent) can be developed using colour developing compositions that do not contain organic solvents such as benzyl alcohol.

Another of the valuable aspects of the present process relates to the alleviation or reduction of pressure and/or stress sensitivity in certain photographic products. This kind of problem is described in J. Soc. Phot., Japan, 22(3), pp. 135—138 (1959); J. Phot. Sci., Vol. 21, pp. 32—38 (1973); J. Phot. Sci., Vol. 21, pp. 221—226 (1973); and Research Disclosure, Vol. 116, pp. 135—137 (1973). The use of hydrophobe-loaded latex compositions in place of conventional solutions of the hydrophobe(s) in the manufacture of photographic products in which such problems had existed can diminish or even eliminate such problems. For example, dyes which have been incorporated as a latex dispersion do not migrate as readily along fracture lines in a photographic material which has been subjected to pressure and/or stress.

Another of the valuable aspects of the present process relates to the surprisingly large quantity of hydrophobic material that can be incorporated into polymeric latex particles thereby. Thus, whereas methods have existed heretofore to manufacture latexes having hydrophobic materials such as plasticizers, developing materials and alkali soluble colour-forming couplers closely associated therewith, the relative amounts of hydrophobe that were incorporated into the latexes thereby were very small (U.S. 3,518,088 and 3,438,920 and 2,772,163), as compared with the amount that can be incorporated into the loadable polymeric latex particles by the process of the present invention. Also, the amount of time required to incorporate hydrophobic material into latexes has been drastically reduced by the present process. For example, liquid plasticizers have been incorporated into polymeric latex particles heretofore by mixing together the oily plasticizer with the latex for an extended time of many hours (U.S. 3,438,920). This method resulted in the incorporation of relatively small amounts of plasticizer, using an extremely lengthy process. By comparison, the present process can result, if desired, in the incorporation (into the latex particles) of an amount of hydrophobe more than equal, by weight to the weight of polymeric latex, if desired, in an extremely short process period. Preferred loaded polymeric latex compositions of the present invention contain from about 25 to about 60 weight percent of hydrophobic material (such as colour-forming coupler, for example), based on the dry weight of the loaded latex composition.

With respect to the process of the present invention, the order of addition of the loadable polymeric latex into the solution of hydrophobe dissolved in water-miscible solvent is very important. Reversing the order results in the coagulation and settling out of the latex or the accumulation of a large proportion of the hydrophobe outside the latex particles in a much less desirable or less useful form. A process wherein streams of the hydrophobe solution and the loadable latex are blended is described and claimed in our copending application No. 37435/75 (Serial No. 1,504,949).

In the manufacture of the loaded latex compositions of this invention, the relative volume of (a) loadable polymeric latex and (b) solution of hydrophobic material(s) in water-miscible solvent which are intermixed in the required manner are not believed critical insofar as the successful practice of the invention is concerned. Thus, so long as some loadable latex particles are present in the solution during that interval of time in which the hydrophobe is forced out of solution because of the increasing hydrophilicity of the solution, some loaded latex particles will be created. For example, one embodiment of the present generic process involves, stepwise, (a) the introduction of a quantity of loadable latex which is not sufficient to affect the hydrophilicity of the solution of hydrophobe to the extent necessary to force the hydrophobe out of solution, and (b) adding enough water to the resulting mixture to affect the desired transfer of hydrophobe from the water-miscible solvent into the latex particles. In this way, loaded latex compositions containing relatively larger proportions of hydrophobe per particle can be made using a relatively dilute solution



of hydrophobe. Thus, it can be seen that there is more than one technique whereby the necessary increase in the hydrophilicity of the solution of hydrophobe can be obtained. The phrase "at least sufficient additional water to cause the hydrophobic compound to become insoluble in the aqueous medium" refers to water additional to that forming the aqueous portion of the loadable polymer latex and includes water in the form of a solution of one or more dissolved salts or other compounds.

However, it is generally preferred that when the dispersed phase polymer solids of the loadable polymeric latex is above 10 weight percent, the relative amount of hydrophobe solution that is blended with such latex should be between 50 and 200 parts by volume per 100 parts of loadable polymeric latex; and still more preferably, one part by volume of hydrophobe solution per part of loadable polymeric latex, particularly when the latex contains from about 12 to 20 weight percent of polymeric particles. Although the actual optimum amount of time necessary to carry out the gradual mixing of the latex and hydrophobe solution in accordance with the present processes will vary in any given instance, depending upon such factors as (a) the types of polymeric latex, hydrophobe and water-miscible solvent, (b) the relative concentrations of hydrophobe and polymeric dispersed phase in the respective materials to be mixed, as well as (c) the relative amounts of latex and hydrophobe solution, it is generally preferred that the gradual intermixing of loadable polymer latex into the hydrophobe solution take place over at least 10 seconds, particularly in those instances in which the polymeric solids content of the loadable polymeric latex is above 12 weight percent. Too fast intermixing has been found to result in formation of a second solid phase in the system and/or coagulation or settling of the latex particles. Such gradual intermixing over at least 20 seconds is still further preferred, especially a period of from 20 to 60 seconds.

After a loaded latex composition has been formed initially, some or all of the water-miscible organic solvent may optionally be removed from the composition without harming the valuable utility of such loaded latex composition. Removal of water-miscible organic solvent may preferably be accomplished by evaporation under any of a wide variety of conditions (at temperatures below about 40°C, for example), preferably under reduced pressure. Preferably at least about half of the water-miscible solvent is removed from the initial compatible blend to thereby form one of the preferred useful loaded latex compositions of the present invention. The preferred photographically useful loaded latex compositions retain their latex characteristics; that is, they have an aqueous continuous phase which optionally contains some of the water-miscible organic solvent (but preferably not more water-miscible solvent than about 30 weight percent of said continuous phase), and a dispersed phase comprising loaded latex particles. The organic solvent and/or some water can be removed from the initial blend of latex plus water-miscible solvent, resulting in a higher "solids" loaded latex. When it is desired to improve the stability of a loaded latex composition to thereby inhibit the tendency of the latex to gradually settle out upon prolonged storage, the composition can be mixed with an aqueous solution of a hydrophilic colloid such as gelatin e.g. an at least 1% gelatin solution. A preferred minimum amount of hydrophilic colloid in the resulting mixtures is about 1 weight percent based on the loaded latex composition, although much more hydrophilic colloid can be used, if desired, to form a stabilized latex product. Preferably the weight ratio of gelatin to polymer on a dry basis in the final composition is from 1:20 to 20:1.

If desired, a stabilized loaded latex product such as those just described can be coated directly on a support by conventional means. Then a substantial amount (generally at least about half, but preferably at least 80 weight percent) of the water in the resulting coated wet layer is removed (preferably by evaporation) from said coated wet layer to form the desired coated substrate product. Many other materials can be present in the coating compositions of this invention in addition to the hydrophilic colloid and the particles of photographically useful loaded latex. For example, photosensitive silver halide particles, sensitizing dyes, antifoggants and coating aids can be blended with any of the compatible blends or photographically useful loaded latex compositions described above to produce useful coating compositions for certain purposes, depending upon the desired composition of the resulting coating on the final coated substrate product. Generally in order to prepare a useful coating composition containing such additional materials, aqueous dispersions and/or solutions of the additional materials can simply be intermixed in appropriate proportions with one of the compatible blends or one of the photographically useful loaded latex compositions of this invention preferably a short time before the resulting coating composition or photographic emulsion is to be coated onto the substrate.

Any coating technique involving the use of coating hoppers and/or other apparatus that can be used to coat conventional photographic emulsions on conventional photographic supports can be used to apply one or more layers of the compositions made by the method of the present invention to a support. Useful coating techniques and supports are described in the publications described in Product Licensing Index, Vol. 92, page 109, December 1971.

The present process for manufacturing loaded latex compositions, and for incorporating the resulting composition into a layer which contains at least one hydrophilic colloid, can be practiced at temperatures ranging from 0°C to 40°C or more, care being necessary merely to prevent, or encourage, as desired or necessary, the setting up or gelling of the coating composition, although it is generally preferred to carry out the imbibition step of the present process at about 25°C or higher. It has been observed that in certain circumstances, usually when loadable polymeric latexes which contain relatively harder polymeric particles (i.e., those loadable latexes having relatively higher Tg's), the latex particles can be made more receptive to the hydrophobic material if relatively higher temperature, such as about 30°C or higher are used during the imbibition step of the present process.

Although in the following Examples, the use of only a few loadable polymer latexes, a few hydrophobic compounds and a few water-miscible organic solvents are described, it should be understood that the techniques and materials set out below are intended to be merely illustrative of how to make and use the compositions and process of this invention. Where appropriate, hydrophobic compounds set out hereinbefore can be used in a manner similar to those described below.

#### Manufacture of a Loadable Polymeric Latex

The following is intended to illustrate one method for manufacturing some of the preferred loadable latexes of this invention.

Into a solution of the following:

- 1 g. Triton 770 (an alkylaryl polyether sulphate, sodium salt, surfactant sold by Rohm & Haas Co.)
- 0.5 g. potassium peroxydisulphate
- 0.1 g. sodium pyrosulphite

in 200 ml water at a temperature of 95°C in a polymerization flask were simultaneously blended, over a period of 20 minutes with continuous stirring, a mixture of 85 g. sec-butyl acrylate plus 5 g. 2-acetoacetoxyethyl methacrylate, a mixture of 10 g. of 3-methacryloyloxypropane-1-sulphonic acid, sodium salt plus 0.15 g. of sodium pyrosulphite, and 100 ml 95°C water. Stirring was continued for 70 minutes after completion of the addition while the reactants were maintained at a temperature of 95°C. The resulting latex product was cooled and then dialyzed for about 16 hours against flowing distilled water in a conventional dialyzer. The percent of solids of the resulting polymeric latex was 9.5%. The latex was "loadable", in accordance with the "Loadable Polymer Latex Test" set out above. By varying the relative amounts of monomeric reactants and water, loadable latexes of varying solids content can be made.

#### Test of Prior Art Latex

In an attempt to determine whether the latex used in U.S. Patent 2,772,163 was "loadable" in accordance with the definition herein, the following test was performed:

Into a container in which 100 parts by volume of acetone was being stirred was gradually, over a period of about 20 seconds, blended an aqueous latex comprising particles in the dispersed phase which was made by the emulsion polymerization of a mixture of 58.8% n-butyl acrylate, 25.2% styrene and 16% methacrylamide, as in Example 1 of U.S. Patent 2,772,163 and U.S. Patent 2,739,137. The solids content of the latex was 11.8%. Within a few minutes, a large portion of the latex had become agglomerated and settled out of the suspension, thereby indicating that the latex was not a "loadable polymeric latex".

#### Example 1

To a solution of 10 g. of the yellow colour-forming coupler, alpha - 4 - (4 - benzyloxyphenylsulphonyl)phenoxy - alpha - pivalyl - 2 - chloro - 5 - [gamma - 2,4 - di - tert - amylphenoxy]butyramido] - acetanilide, dissolved in 160 ml. of acetone was gradually stirred, over about a one-minute period of time, 90 g. of loadable polymer latex like that described above, except that the latex had 11.3% solids (deter-

mined after drying at 110°C). After the loadable latex was blended with the coupler solution (thereby forming a compatible blend), most of the acetone was removed by evaporation (in a rotary evaporator at 40°C). The resulting coupler-loaded latex composition did not coagulate upon storage, and after being coated and dried on a transparent photographic support, yielded a transparent layer. The coupler loaded latex composition was also compatible with gelatin.

#### Example 2

Example 1 was repeated, except that the coupler in this example was alpha - pivalyl - alpha - (4 - carboxyphenoxy) - 2 - chloro - 5 - [gamma - (2,4 - di - tert - amylphenoxy)butyramido] - acetanilide. Practically identical results were obtained.

#### Example 3

Example 1 was repeated, except that the coupler in this Example was the cyan colour-forming coupler, 2 - [alpha - (2,4 - di - tert - amylphenoxy)butyramido] - 4,6 - di - chloro - 5 - methylphenol. Practically identical results were obtained.

#### Example 4

##### Evaluation In Photographic Material

Using the coupler loaded latex compositions from Examples 1, 2 and 3 above, photographic emulsions were prepared by simply blending each of the coupler-loaded latex compositions with appropriately sensitized silver halide emulsions as follows:

A. The loaded latex composition produced in Example 3 was blended into an otherwise conventional red-sensitized gelatino silver halide emulsion. The resulting emulsion was coated on a conventional photographic polymeric film support to yield a dried layer containing the following ingredients:

coupler=8.5 mg/dm<sup>2</sup>  
silver=3.7 mg/dm<sup>2</sup>  
gelatin=32.1 mg/dm<sup>2</sup>

B. The coupler-loaded latex composition produced in Example 1, above, was blended into an otherwise conventional blue-sensitive gelatino silver halide emulsion. The resulting emulsion was coated as in part A, above, to yield a dried layer containing the following ingredients:

coupler=7.1 mg/dm<sup>2</sup>  
silver=3.8 mg/dm<sup>2</sup>  
gelatin=11.7 mg/dm<sup>2</sup>

C. An emulsion was prepared as in part B above, using the coupler-loaded latex composition of Example 2 using an otherwise conventional green sensitized gelatino silver halide emulsion.

D. Each of the photographic coatings described above was exposed and developed in a conventional manner to determine its relative speed, Dmax, gamma and Dmin. A control coating prepared by coating and drying the emulsion without coupler-loaded latex composition but containing the same amount of the same coupler dissolved in dibutyl phthalate (a conventional coupler solvent) at a coupler: solvent weight ratio of 1:1 was evaluated in each instance. Results from developing the exposed coatings are set out in Table 1, below:

TABLE 1

Sample	Relative Speed	Dmax	Gamma	Dmin
A-coupler-loaded latex product	257	2.84	3.16	0.05
A-control	282	2.97	3.13	0.05
B-coupler-loaded latex product	69	1.42	2.33	0.05
B-control	46	1.15	1.13	0.05
C-coupler-loaded latex product	80	1.77	3.13	0.05
C-control	76	1.67	2.93	0.05

Colour processing sequence at 24°C and solutions used are given below

Colour Development Sequence				
5	Prebath	10 seconds	5	
	Rinse	10 seconds		
	Developer	8 minutes		
	Rinse	10 seconds		
	Fix	2 minutes		
10	Wash	1 minute	10	
	Bleach	6 minutes		
	Wash	2 minutes		
Solution Make-Up For Colour Development				
Prebath				
15	Water	800.0 ml	15	
	Borax (Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O*)	20.0 grams		
	Sodium sulphate, desiccated	100.0 grams		
	Sodium hydroxide, cold 10% solution	10.0 ml		
	Water to make	1.0 litre		
20	pH (21°C),	9.30 ± 0.1	20	
	Specific gravity (21°C),	1.096 ± 0.004		
Colour Developer				
25	Water, about 21—24°C	800.0 ml	25	
	Sodium hexametaphosphate	2.0 grams		
	Sodium sulphite, desiccated	4.0 grams		
	2-amino-5-diethylamino-toluene monohydrochloride	3.0 grams		
	Sodium carbonate, monohydrated	20.0 grams		
30	Potassium bromide or Sodium bromide	2.0 grams	30	
	Water to make	1.7 grams		
	pH (21°C)	1.0 litre		
	Specific gravity (21°C),	10.63 ± 0.05		
		1.023 ± 0.003		
Fixing Bath				
35	Water, about 50°C	600.0 ml	35	
	Sodium thiosulphate (hypo)	240.0 grams		
	Sodium sulphite, desiccated	15.0 grams		
	Acetic acid, glacial	13.4 ml		
	Boric acid, crystals	7.5 grams		
40	Potassium alum	15.0 grams	40	
	Water to make	1.0 litre		
	pH (21°C),	4.25 ± 0.25		
	Specific gravity (21°C),	1.150 ± 0.005		
Bleach Bath				
45	Water, about 21°C	800.0 ml	45	
	Potassium bromide or Sodium Bromide	20.0 grams		
	Potassium Dichromate	17.0 grams		
	Potassium alum	5.0 grams		
	Water to make	40.0 grams		
50	(Adjust pH to 3.1 ± 0.20 (21°C) with 10% sodium hydroxide solution or 7N sulphuric acid)	1.0 litre	50	
	Specific gravity (21°C),	1.036 ± 0.003		
55	E. Results from processing another sample of the same coatings tested under part "D" above using a cobalt hexammine amplifier-developer in accordance with the			55

disclosure of Example 1 of U.S. Patent 3,765,891 (British Specification 1,399,481) are set out in Table 2 below.

TABLE 2

	Sample Tested	Relative Speed	Dmax	Gamma	Dmin	
5	A-coupler-loaded latex product	525	3.46	4.56	0.08	5
	A-control	562	3.56	4.43	0.11	
10	B-coupler-loaded latex product	795	1.47	1.63	0.08	10
	B-control	832	1.33	1.30	0.08	
	C-coupler-loaded latex product	1107	1.80	1.50	0.08	
	C-control	1123	1.74	1.90	0.08	

15 Note that in these Examples, the coupler-loaded latex compositions of this invention were dispersed in the photographic emulsions described above without the aid of high energy milling and without the necessity for a long, time consuming incorporation and dispersion procedure of any kind, but that results shown in Tables 1 and 2 indicate that products made by the present invention are acceptable and comparable to conventional colour photographic products.

20 One apparently unique property which has been observed with respect to the coupler-loaded latex composition aspect of this invention relates to the surprising availability of the coupler for reaction with oxidized colour developer during colour development. For some reason which has not yet been ascertained, colour-forming couplers are reactive with colour developers to a surprising extent even though they are contained in the polymer particles of the latex. Also, when the present invention is practiced with couplers as described above, considerably more uniform distribution of the couplers through the gelatin layers is obtained than can ordinarily be obtained using conventional coupler dispersion techniques. Consequently, after colour development, the resulting dyes are more uniformly distributed through their respective layers in the finished coloured photographic materials.

25 In the following several Examples, the present invention is illustrated with respect to an embodiment of this invention that shall be referred to as "RDR-loaded latexes" wherein RDR symbolizes one or more redox dye releasers. It is known that redox dye releasers are compounds which can be oxidized by oxidized developing agents. For example, they can be cross-oxidized to provide a species which, as a function of oxidation, will release a diffusible dye such as by alkaline hydrolysis. Such redox dye releasers are described in U.S. Patents 3,725,062, 3,698,897, and 3,628,952 and British Specifications 1,405,662, 1,458,471, 1,464,104, 1,464,105, 1,465,183 and 1,465,184.

30 RDR-loaded latex compositions can be manufactured using a manipulative procedure like that set out in Example 1, wherein an appropriate water-miscible organic solvent medium is used, the particular solvent(s) depending upon the solubility characteristics of the particular hydrophobic RDR compound(s) selected.

#### 45 Example 5

In this Example, the preparation of a hydrophobic RDR-loaded latex composition is illustrated, along with its use in the manufacture of a photographic material. The material prepared using the RDR-loaded latex composition is compared with an otherwise identical material made using the RDR compound conventionally incorporated by conventional coupler solvent techniques.

#### A. Manufacture of RDR-loaded Latex Composition

55 Twelve grams of RDR compound (identified below) were dissolved in 240 ml tetrahydrofuran by stirring them together at room temperature. Then, with continued moderate stirring, 150 grams of a loadable polymeric latex (identified below) were gradually blended into the resulting solution. The resulting loaded polymeric latex composition of solvent and RDR-loaded latex were then placed into a rotary evaporator. Under vacuum at 50°C, all but about 1 weight percent of the tetrahydrofuran was then removed. The resulting composition was filtered through Reeve Angel Grade 230 filter paper. The filtrate (dispersion of RDR-loaded latex particles) was made up to 200 grams total weight and 34 grams of a 35 weight percent gelatin solution (50°C) were blended into it. The resulting stabilized loaded latex composition

was then chill set and refrigerated until it was used as a component in a coating composition.

#### B. Photographic Material

Details relating to quantities of materials and the like in the various layers of a photographic material having the following layer arrangement can be found in U.S. patent No. 3,928,312.

- (a) Transparent Emulsion Cover Sheet
- (b) Gelatin Overcoat Layer
- (c) Red Sensitive Emulsion
- (d) RDR-Loaded Latex Composition
- (e) Carbon + Gelatin
- (f)  $\text{TiO}_2$  + Gelatin
- (g) Mordant + Gelatin
- (h) Transparent Poly(ethyleneterephthalate) Support

In layer (d) was coated the stabilized RDR-loaded composition made in accordance with part A of this Example, wherein the RDR compound was the cyan dye releasing redox compound, N - [4 - (2,4 - di - tert - pentylphenoxy)butyl] - 1 - hydroxy - 4(3 - [5 - hydroxy - 6 - (2 - methyl sulphonyl - 4 - nitrophenylazo) - 1 - naphthylsulphanoyl]benzenesulphonamido) - 2 - naphthamide, and the loadable latex was a copolymer latex made by free radical emulsion polymerizing 85 parts by weight of n-butylacrylate, 10 parts by weight of sodium 3-methacryloyloxypropane-1-sulphonate and 5 parts by weight of 2-acetoacetoxyethyl methacrylate. In the stabilized RDR-loaded latex composition which was coated to form layer (d) the weight ratio of RDR compound to latex polymer to gelatin was such that the resulting layer contained 0.54 g RDR compound, 0.54 g latex copolymer and 1.08 g gelatin per square metre.

#### C. Control

A material like that described under B of this Example was prepared so that it was substantially identical to that prepared above with the exception that, rather than an RDR-loaded latex composition, a conventional organic solvent/gelatin dispersion was used to make layer (d), with gel and RDR levels being the same as that described under B of this Example. The solvent was 1,4-cyclohexylenedimethylene bis(2-ethylhexanoate) at a level of 0.27 g/m<sup>2</sup> in the layer.

#### D. Comparative Test

Each of the materials from B and C of this Example was exposed (1/100 sec.) to a tungsten light source through the transparent cover sheet and a graduated density test object filtered for red light. A conventional viscous alkaline processing composition containing carbon was spread from a pod between the photosensitive material and the transparent cover sheet at about 22°C by passing the diffusion transfer "sandwich" between a pair of juxtaposed rollers so that the layer of liquid processing solution was 0.005 inch thick. Upon development, the resulting cyan test image in the mordant (layer g) yielded the following sensitometric data:

		Relative*				
		Speed	Contrast	Dmin	Dmax	
45	Example 4	110	1.39	0.20	1.91	45
	Control	100	1.42	0.22	1.96	

\*Measured at 1.0 above Dmin.

Note that almost identical sensitometric results were obtained.

#### Example 6

In addition to being more readily and uniformly dispersible through hydrophilic colloid coating layers in the form of hydrophobe-loaded latex, some of the hydrophobic materials exhibit unexpected capabilities when they are incorporated into layers in this form. An example of such unexpected capabilities is illustrated in the following Example, with respect to an ultraviolet absorbing compound. Note that in this instance, the use of a UV absorber-loaded latex composition in accordance with this invention resulted in surprisingly high optical densities and an unexpected, valuable sharp "cut-off" at about 415 nm.

- 5 A. A UV absorber-loaded latex composition was prepared by first dissolving 40 g of 3-diethylaminoallylidene malonitrile in 400 cc of acetone, and then gradually stirring into the resulting solution 1320 g of the aqueous latex, poly-(n-butyl methacrylate-co-2-acrylamido-2-methylpropane sulphononic acid-co-2-acetoacetoxyethyl methacrylate (85:10:5 weight ratio) at 9.5% total solids. The acetone was then stripped from the resulting blend by treating it at 50°C in vacuum for about 24 minutes. The resulting latex composition was then blended into an aqueous gelatin solution, coated onto a transparent photographic support and dried. Coverages of gelatin and UV absorber in the resulting coating are set out in Table 3, below.
- 10 B. For comparison, an equivalent amount of the same UV absorber used in part of this Example was dispersed into a gelatin solution by means of a colloid mill. The A UV absorber is liquid at room temperature. Amounts of gel and UV absorber were used to yield the same coverages in the resulting coated layer as that made according to part A of this Example.
- 15 C. In another comparative experiment, the same UV absorbing compound used in parts A and B of this Example was first dissolved in an equal volume of di-n-butylphthalate high boiling solvent. Then the resulting solution was dispersed in an aqueous gelatin solution using a colloid mill in the conventional manner. Coatings of the resulting dispersion on the transparent photographic support were made to yield dried coverages as set out in Table 3, below.
- 20

TABLE 3

Coating	Gelatin g/m <sup>2</sup>	UV absorber g/m <sup>2</sup>	Optical Densities	
			370 nm	415 nm
Control	0.54	0	0.08	0.05
Part B	0.54	0.20	1.16	0.55
Part C	0.54	0.20	1.60	0.42
Part A	0.54	0.20	3.00	0.11

25 This data demonstrates that loaded latex compositions which are charged with this type of UV absorber can yield unexpected and valuable results, including unexpectedly high levels of ultraviolet light absorbancy and surprisingly sharp cut off of absorption in the visible region of the spectrum.

30

## Example 7

- 35 In this Example the manufacture of a photographic material incorporating a filter dye by the process of this invention is demonstrated.
- 40 Using the conventional layer format described in British Patent No. 923,045 and U.S. Patent No. 3,046,129, colour photographic materials were prepared in which a filter layer was present between the blue sensitive layer and a fast green-sensitized layer. The colour-forming layers of these materials contained conventional incorporated couplers. Except for the filter layer, all of the test materials of this Example were substantially the same. In one "control" material, Carey-Lea colloidal silver was used. In a second material, a conventional mordanted filter dye was used. In a third material, a filter dye-loaded latex (ca. 35% filter dye) composition was used. Data relating to coverages of materials in the filter layer appear in the following Table. Identification of the various materials used in the filter layer appear immediately following the Table.
- 45

TABLE 4  
Evaluation of Filter Dyes

Material	Gelatin*	Carey-Lea Silver*	Dye I*	Mordant*	Dye II*	Latex*	Rel.** Blue Speed	λ <sub>max</sub>
A.	0.98	0.054	—	—	—	—	100	428
B.	0.98	—	0.074	0.086	—	—	73	448
C.	0.98	—	—	—	0.086	0.26	82	450

\*coverage in g/m<sup>2</sup>. \*\*Blue Speed measured at 1.0 above D<sub>min</sub>.

- 55 Dye I—4 - [(3 - ethyl - 2 - benzoxazolyldene)ethylidene] - 3 - methyl - 1 - (p - sulphophenyl) - 2 - pyrazolin - 5 - one, monosulphonated—U.S. Patent 3,282,699
- 60 Dye II—p-diethylamino-2-(4-hexenesulphonylamino benzoyl)-cinnamonnitrile  
Mordant—poly(α-methylallyl-N-guanidylketimine)—U.S. Patent 3,282,699  
Latex—poly(n - butylmethacrylate - co - 2 - acrylamido - 2 - methylpropane-sulphonic acid - co - 2 - acetoacetoxyethylmethacrylate (85:10:5 weight ratio))

The filter dye-loaded latex composition used in this test was prepared by (a) diluting 9.5 g of latex (15.2% solids) with 55 ml. water, (b) then gradually over a period of about a minute blending the dilue latex into a solution of 0.48 g. of the filter dye dissolved in 50 ml. tetrahydrofuran, (c) in a rotary evaporator at 40°C, removing the tetrahydrofuran, and (d) then blending into the resulting loaded latex composition 267 ml. of aqueous 2.5% gelatin and 5.3 ml. of saponin (15% in water).

In order to obtain the "relative blue speed" figures for the above Table, the dried coated materials were exposed for 1/100 second to a 500 watt tungsten lamp which had been adjusted to a colour temperature of 3200°K. The exposed materials were then subjected to a conventional reversal colour process like that described in U.S. Patent No. 3,046,149.

The results of this Example demonstrate that filter dye-loaded latex compositions, prepared in accordance with the process aspect of this invention can be used advantageously as a replacement for Carey-Lea silver as a filter for blue light in photographic materials. Note that significantly less desensitization of the blue sensitive emulsion layer occurred when the loaded latex composition of this invention was used, as compared with the use of a conventional mordanted filter dye.

#### Example 8

In this Example, the use of a loaded latex composition wherein the latex particles are loaded with a photographic sensitizing dye is illustrated.

#### A. Control-Dye Dissolved in Methanol for Dispersion

A photographic material suitable for alkaline vapor processing was prepared by coating a layer comprising

- a) a conventional sulphur, gold and reduction sensitized silver bromide emulsion,
- b) a spectral sensitizing dye, anhydroy-3,9-diethyl-5,5'-dimethoxy-3'-3-(3-sulphopropyl)thiacarbocyanine hydroxide dissolved in methanol,
- c) ascorbic acid,
- d) an antifoggant, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene,
- e) an image stabilizer precursor, 3-s-thiuronium-1-methylpropane sulphonate,
- f) an incorporated developer 1,2,3,4-tetrahydro-1,4-methanonaphthalene-5,8-diol and
- g) a hardener, bis(vinylsulphonylmethyl)ether

at 27.98 mg silver/dm<sup>2</sup> and 96.84 mg gelatin/dm<sup>2</sup> on a polyethylene terephthalate film support. The material was exposed for 30 seconds to tungsten light (500W, 3000°K), subjected to methylamine vapour for 30 seconds and washed for 5 minutes with distilled water. The sensitometric results are shown below.

#### B. Sensitizing Dye Dispersed Via a Loaded Latex Composition

##### 1. Preparation of Dye-Loaded Latex Composition

The following ingredients were used in this part of this Example:

- (a) 350 mg of the same sensitizing dye used in part A of this Example,
- (b) 350 ml methyl alcohol
- (c) 17 ml water
- (d) 175 ml of a 10.3% solids loadable latex consisting of copoly(n-butyl acrylate/3-methacryloyloxypropane-1-sulphonic acid, Na salt/2-acetoacetoxyethyl methacrylate) (85:10:15 weight ratio)
- (e) 17.5 ml of a 10 weight percent solution of gelatin in water

Initially, (d) was gradually stirred into a solution of (a) dissolved in a mixture of (b) plus (c). After (e) was stirred into the resulting compatible blend, the resulting stabilized loaded latex composition was then subjected to a vacuum stripping step in a conventional laboratory scale rotary evaporator to remove substantially all the methyl alcohol. The vacuum stripped product was then incorporated into an emulsion otherwise just like that of part A of this Example. The resulting emulsion was coated as in part A on a polyester film support and dried down in a conventional manner to form a photosensitive element. This element was subjected to the same test as was that of part A of this Example.

#### C. Test Data and Results

The coatings of parts A and B of this Example were exposed, processed and washed as in Part A, above. Some of the sensitometric properties of the processed films were:



	Sample	Relative Speed	Gamma	Dmin	
	A-control	100	6.80	0.06	
5	B-loaded latex product	100	6.47	0.06	5

These results demonstrate that, surprisingly, the latex compositions of this invention loaded with a sensitizing dye can function well in a photographic material and can be used in place of an alcohol solution of the sensitizing dye as an effective means for dispersing such dye through a photographic silver halide emulsion layer. The present method is advantageous in that it makes it possible to remove the alcohol prior to the time the sensitizing dye is dispersed into a photographic emulsion layer. With certain sensitizing dyes, this advantage is more pronounced than others, depending upon the relative solubility of the dye in the alcohol.

#### Example 9

In this Example, the use of the present process to prepare pesticide-loaded latex compositions is illustrated.

##### A. Methyl Parathion

Fifteen grams of commercial methyl parathion (20% methyl parathion+80% xylene) were dissolved in 150 ml. acetone. Into this solution, at room temperature, were gradually blended, with continuous stirring, 200 grams of a dilute latex which was prepared by diluting 66 grams of an 18.25% solid loadable polymeric latex with enough water to produce 200 grams of dilute latex. The loadable polymeric latex had been prepared by polymerizing a mixture of 50 parts by weight of n-butyl methacrylate, 40 parts by weight of styrene and 10 parts by weight of 2-acrylamido-2-methyl propane sulphonic acid in accordance with the above-described procedure.

The resulting loaded latex/solvent mixture was then placed in a 2000 ml. flask, in which it was subjected to evacuation for 15 minutes at about 50°C to remove organic solvent. The resulting methyl parathion-loaded latex composition was then filtered (no residue was observed) to yield a homogeneous dispersion which was stable and did not visibly settle spontaneously (upon storage at room temperature) for many weeks. The product contained particles which apparently contained polymer and pesticide in a weight ratio of about 1:1.

##### B. Parathion

Part A, above was repeated, using the following materials:

35	parathion	7.1 g	35
	acetone	150 ml	
	18% solids latex	45 g	
	water (for latex)	108 ml	

The resulting loaded latex had a polymer to pesticide weight ratio of about 8 to 7, respectively. By weight, the parathion content of the loaded latex product was 5.5%. This product could be readily diluted with water for conventional spray application to agricultural plants.

#### Example 10

In this Example, the use of the present process to prepare fluor-loaded latex compositions is illustrated. The fluor is a blend of two hydrophobic materials which, co-operatively, serve as aids for scintillation counting. Scintillation counting is useful in the detection and measurement of relatively low levels of radioactivity, and finds application in the field of radioactive tracing. In this example, the fluor composition is a blend of 2,5-diphenyloxazole (PPO) and 2,2'-p-phenylenebis(5-phenyloxazole) (POPOP). Both of these materials are hydrophobic.

Three grams of PPO and 15 mg. of POPOP were dissolved in 90 ml. tetrahydrofuran (THF). Then, at room temperature, 90 g. poly(n-butylmethacrylate-co-styrene-co-acrylamido-2-methylpropane sulphonic acid) (50:40:10 weight ratio) aqueous latex containing 9 g. of polymer, was blended slowly into the solution of fluor dissolved in THF. Then the solvent was removed by evaporation in a conventional rotary evaporator. After filtration, 25 g. of a 10% gelatin solution was blended into the fluor-loaded latex composition. The final gel stabilized composition contained 3% PPO,  $1.5 \times 10^{-2}$ % POPOP, 9% polymer and 2.5% gelatin.

This composition was coated at a coverage of 10 ml./100 cm<sup>2</sup> on a conventional transparent subbed poly(ethylene terephthalate) photographic support and then dried. Three strips (2''×1/2'') were cut from the resulting dried scintillation counting element and treated with (a) 0.01 ml. benzoic acid-<sup>3</sup>H solution in water, (b) 0.01 ml. benzoic acid-<sup>3</sup>H solution in p-dioxane, and (c) 0.01 ml. benzoic acid-<sup>14</sup>C in water, respectively. (Each solution was equivalent to approximately 22,000 disintegrations per minute). The strips were dried, mounted in 20 ml. glass counting vials and counted at 12°C in a Packard Tri-Carb Liquid Scintillation Counter, Model 3380. The strips were aligned normal to the axis of the two photomultiplier tubes. "Counting efficiency" was determined by comparing the detected emission with the theoretical disintegrations in a given period of time. Results of these tests are set out in the following Table:

TABLE

Sample	Material Measured	Counting Efficiency
a	<sup>3</sup> H benzoic acid (H <sub>2</sub> O)	—
b	<sup>3</sup> H benzoic acid (p-dioxane)	31.8%
c	<sup>14</sup> C benzoic acid (H <sub>2</sub> O)	25.6%
		89.5%

These counting efficiencies are considered to be unusually high for solid scintillation counting compositions or elements. The high counting efficiency is believed at least partly due to the fact that the fluor is distributed uniformly and in the form of a loaded latex.

## WHAT WE CLAIM IS:—

1. A method of making an aqueous loaded polymer latex, of which the dispersed phase comprises a polymer and a hydrophobic compound (as defined herein), which comprises the step of adding to a solution of the hydrophobic compound in a water-miscible organic solvent (as defined herein), an aqueous loadable polymer latex (as defined herein) and, if required, at least sufficient additional water to cause the hydrophobic compound to become insoluble in the aqueous medium so formed so that the loaded polymer latex is formed.

2. A method as claimed in Claim 1 in which the loadable latex and additional water (if used) is added over a period of at least 10 seconds.

3. A method as claimed in Claim 1 in which the loadable latex and additional water (if used) is added over a period of from 20 to 60 seconds.

4. A method as claimed in any of Claims 1—3 in which all the necessary water is contained in the loadable polymer latex.

5. A method as claimed in any of Claims 1—4 in which the amounts of hydrophobic compound and loadable latex are chosen so that the loaded polymer particles contain from 2 to 300 parts by weight of hydrophobic compound per 100 parts by weight of polymer.

6. A method as claimed in any of Claims 1—4 in which the amounts of hydrophobic compound and loadable latex are chosen so that the loaded polymer particles contain from 5 to 100 parts by weight of hydrophobic compound per 100 parts by weight of polymer.

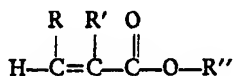
7. A method as claimed in any of Claims 1—6 in which, after the formation of the loaded polymer, at least half of the water-miscible organic solvent is removed from the latex.

8. A method as claimed in any of Claims 1—7 in which the loadable polymer latex is compatible with gelatin solutions.

9. A method as claimed in any of Claims 1—8 in which the loadable polymer comprises a copolymer of at least two ethylenic monomers, from 2 to 25 weight percent of said monomers consisting of a monomer containing a sulphonic acid or sulphonate group.

10. A method as claimed in any of Claims 1—9 in which the loadable polymer is a copolymer prepared from:

(a) 75 to 98 wt. percent of a monomer of the formula:



I

wherein

R is hydrogen or an alkyl group having 1—5 carbon atoms,

R' is hydrogen or a methyl group and

R'' is an aliphatic group having 1—6 carbon atoms, and

- 5 (b) 2 to 25 wt. percent of an ethylenic monomer containing a sulphonic acid or sulphonate group and having a molecular weight of at most 300. 5

11. A method as claimed in any of Claims 1—9 in which the loadable polymer is a copolymer prepared from:

- 10 (a) 80 to 95 wt. percent of a monomer of Formula I as defined in Claim 10, 10  
(b) 2 to 10 wt. percent of an ethylenic monomer containing a sulphonic acid or sulphonate group and having a molecular weight of at most 300, and  
(c) 0.2 to 10 wt. percent of an ethylenic monomer containing cross-linkable groups.

12. A method as claimed in Claim 11 in which the monomer (c) contains as cross-linkable groups, groups containing an active methylene group.

- 15 13. A method as claimed in Claim 11 or 12 in which monomer (a) is methyl, ethyl, propyl or butyl acrylate or methylacrylate. 15

14. A method as claimed in any of Claims 11—13 in which monomer (b) is 2-acrylamido-2,2-dimethylethane-1-sulphonic acid, or 3-methacryloyloxypropane-1-sulphonic acid or salts thereof.

- 20 15. A method as claimed in any of Claims 1—14 in which the water-miscible organic solvent is acetone, ethyl alcohol, methyl alcohol, isopropyl alcohol, methyl ethyl ketone, tetrahydrofuran, dimethylformamide, N-methyl pyrrolidone or dimethylsulphoxide or a mixture of two or more thereof. 20

16. A method as claimed in any of Claims 1—15 in which the loaded latex is mixed with an at least 1 wt. percent gelatin solution after its formation.

- 25 17. A method as claimed in Claim 16 in which the weight ratio of gelatin to polymer on a dry basis in the final composition is from 1:20 to 20:1. 25

18. A method as claimed in any of Claims 1—17 in which the hydrophobic compound is a photographic silver halide developing agent, a colour coupler, a dye-releasing compound, a filter or sensitizing dye or an ultraviolet-absorbing compound.

- 30 19. A method as claimed in any of Claims 1—17 in which the hydrophobic compound is a pesticide or a fluor. 30

20. A method as claimed in any of Claims 1—19 in which the particles of polymer in the loaded latex have an average diameter of 0.02 to 0.2 micron.

- 35 21. A method of making an aqueous loaded polymer latex substantially as described herein and with reference to the Examples. 35

22. An aqueous loaded polymer latex made by the method of any of Claims 1—21.

- 40 23. An aqueous loaded polymer latex of which the dispersed phase comprises a loadable polymer (as defined herein) and a hydrophobic compound (as defined herein) wherein the particles of the dispersed phase have an average diameter of 0.02 to 0.2 micron. 40

24. A loaded polymer latex as claimed in Claim 23 in which the dispersed particles contain from 40 to 300 parts by weight of hydrophobic compounds per 100 parts by weight of polymer.

- 45 25. A loaded polymer latex as claimed in Claim 23 or 24 in which the dispersed particles contain from 40 to 200 parts by weight of hydrophobic compound per 100 parts by weight of polymer. 45

26. A loaded polymer latex as claimed in any of Claims 23—25 in which the loadable polymer and the hydrophobic compound are any of those specified in any of Claims 8—14, 18 and 19 respectively.

- 50 27. A loaded polymer latex as claimed in any of Claims 23—26 which also contains gelatin in an amount such that the ratio of gelatin to polymer on a dry weight basis is from 1:20 to 20:1. 50

28. A loaded polymer latex according to Claim 23 substantially as described herein and with reference to the Examples.

- 55 29. A photographic material comprising a support bearing a photosensitive silver halide layer and a layer obtained from a composition containing a loaded polymer latex according to any of Claims 22—28. 55

30. A photographic material as claimed in Claim 29 in which the hydrophobic compound in the loaded polymer latex is a photographic silver halide developing agent, a colour coupler, a dye-releasing compound, a filter or sensitizing dye or an ultraviolet-absorbing compound.

- 60 31. A photographic material as claimed in Claim 29 or 30 in which the hydrophobic compound in the loaded polymer latex is a photographic colour coupler and 60

in which the ratio of hydrophobic compound to loadable polymer is in the range 1:2 to 2:1 by weight.

32. A photographic material as claimed in any of Claims 29—31 in which the loaded polymer is located in a photosensitive silver halide emulsion layer.

5 33. A photographic material according to Claim 29 substantially as described herein and with reference of the Examples. 5

L. A. TRANGMAR, B.Sc., C.P.A.,  
Agent for the Applicants.

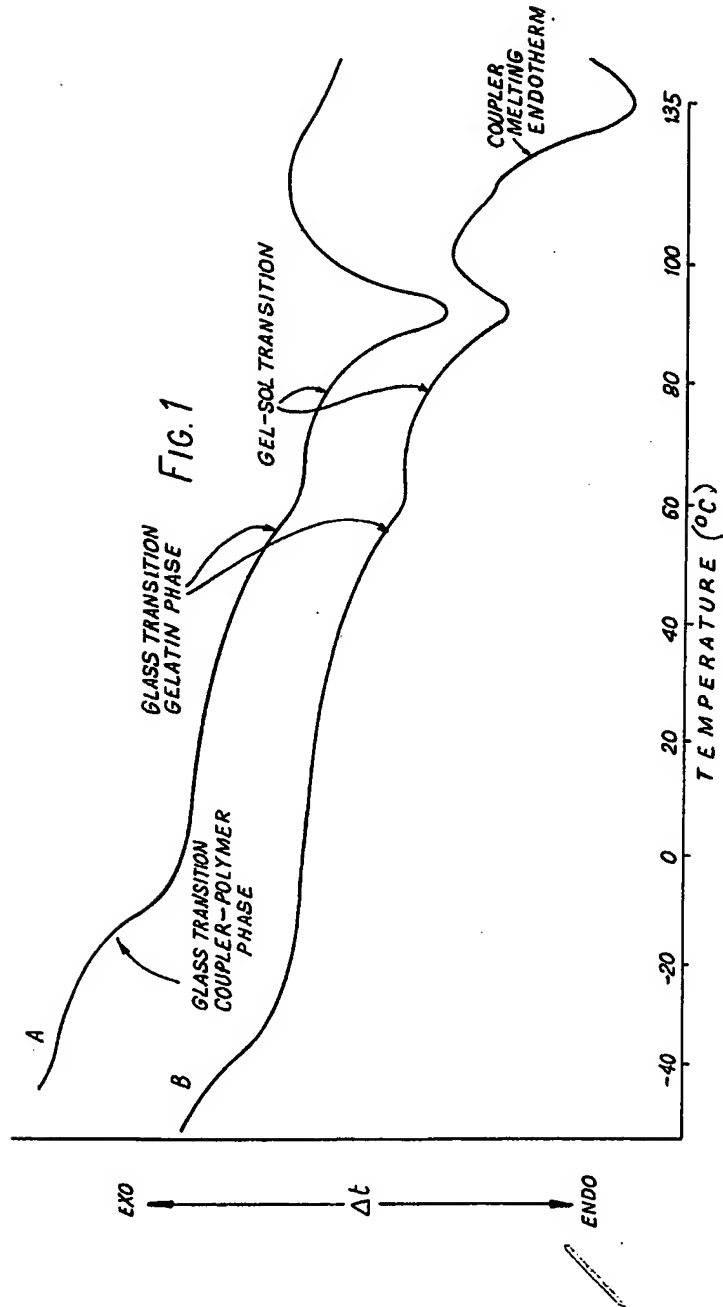
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COMPLETE SPECIFICATION

1 SHEET

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## Attachment D

### METHOD OF MAKING IMPREGNATING POLYMER LATEX COMPOSITION

**Patent number:** JP54032552  
**Publication date:** 1979-03-09  
**Inventor:** FUJIWARA MITSUTO; MATSUO SHIYUNJI; WADA TSUNEO; ABE NAOTO; MASUKAWA TOYOAKI; OOISHI KEIJI; IIJIMA AKIO  
**Applicant:** KONISHIROKU PHOTO IND  
**Classification:**  
- **international:** C08J3/215; G03C7/388; C08J3/20; G03C7/388; (IPC1-7): C08J3/06; G03C1/00  
- **european:** C08J3/215; G03C7/388P  
**Application number:** JP19770098566 19770817  
**Priority number(s):** JP19770098566 19770817

Also published as:

 US4368258 (A1)

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Abstract not available for JP54032552

Abstract of corresponding document: **US4368258**

In the process for preparing impregnated polymer latex compositions by impregnating a hydrophobic substance in dispersed polymer particles in an aqueous polymer latex, the improvement comprises impregnating said hydrophobic substance, wherein the impregnation is effected by mixing said hydrophobic substance which is solid state, a water-miscible organic solvent and aqueous polymer latex wherein a polymer of the polymer latex is prepared from ethene monomers and containing at least one hydrophilic group.

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**Attachment E**

**SILVER HALIDE COLOR PHOTOGRAPHIC SENSITIVE MATERIAL**

**Patent number:** JP2001133931  
**Publication date:** 2001-05-18  
**Inventor:** HOSOKAWA JUNICHIRO; TAMAOKI HIROSHI  
**Applicant:** FUJI PHOTO FILM CO LTD  
**Classification:**  
**- international:** G03C1/76; G03C7/20; G03C1/76; G03C7/20; (IPC1-7):  
G03C1/76; G03C7/20  
**- european:**  
**Application number:** JP19990316942 19991108  
**Priority number(s):** JP19990316942 19991108

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**Abstract of JP2001133931**

**PROBLEM TO BE SOLVED:** To obtain a photosensitive material using silver halide grains having a high silver chloride content, excellent in suitability to rapid processing and having improved pressure resistance. **SOLUTION:** The silver halide color photographic sensitive material has at least one yellow coupler-containing blue-sensitive silver halide emulsion layer, at least one magenta coupler-containing green-sensitive silver halide emulsion layer, at least one cyan coupler-containing red-sensitive silver halide emulsion layer, a 2nd protective layer comprising a non-photosensitive hydrophilic colloidal layer as the top layer and a 1st protective layer adjacent to the 2nd protective layer on the substrate side and adjacent to the blue-sensitive maximum sensitivity layer on the side farther from the substrate on the substrate. Flat platy silver halide grains each having an aspect ratio of  $\geq 2$  and  $\geq 50$  mol% silver chloride content occupy  $\geq 50\%$  of the total projected area of silver halide grains in at least one of the emulsion layers. The elastic modulus of the 1st protective layer is 2-10 times that of the blue-sensitive layer having the maximum sensitivity.

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